

Reversible optical doping of graphene

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Abstract

The ultimate surface exposure provided by graphene monolayer makes it the ideal sensor platform but also exposes its intrinsic properties to any environmental perturbations. In this work, we demonstrate that the charge carrier density of graphene exfoliated on a SiO₂/Si substrate can be finely and reversibly tuned between electron and hole doping with visible photons. This photo-induced doping happens under moderate laser power conditions but is significantly affected by the substrate cleaning method. In particular, it is found to require hydrophilic substrates and to vanish in suspended graphene. These findings suggest that optically gated graphene devices operating with a sub-second time scale can be envisioned but also that Raman spectroscopy is not always as non-invasive as generally assumed.

Optical and electronic properties of graphene can be modulated by continuously tuning the charge carrier density using electrostatic gating¹⁻⁶, electrochemical doping⁷ or charge transfer by adsorption of molecular species⁸⁻²³. Besides electronic transport, the doping of graphene has a marked effect on the fundamental electron-phonon interactions, like the breakdown of the adiabatic Born-Oppenheimer approximation¹⁻⁴, the interplay between adiabatic and non-adiabatic effects²³ or the interference between all the quantum pathways involved in inelastic light scattering⁵. These effects have been conveniently investigated by Raman spectroscopy, which is also sensitive to the number of layers²⁴, their stacking ordering²⁵⁻²⁸, the nature and density of defects²⁹⁻³¹ and the in-plane strain variations^{32,33}. As a consequence, Raman spectroscopy of active modes in graphene, like the G and 2D bands is being considered as a high-throughput technique to characterize graphene and to probe the inelastic light scattering phenomena. Moreover, several groups^{24,34,35} have reported that no significant spectral changes were observed by collecting Raman spectra of graphene exfoliated on SiO₂/Si substrate, with a laser power P_{laser} ranging from 0.04 to 4 mW. Therefore, Raman spectroscopy is considered as non-invasive when performed with P_{laser} in the mW range.

Yet, the non-invasive character of Raman spectroscopy has been questioned by the reports of possible photo-induced effects and some authors recommended to use more cautious experimental conditions (laser power limited to 70 μW ³⁶ or Ar annealing³⁴). Laser irradiation has even been shown to induce irreversible damages of graphene^{37,38}. Interestingly, we have found that the charge carrier density of exfoliated graphene lying on a hydrophilic SiO₂/Si substrate can be finely and reversibly tuned optically with visible photons. The influence of the laser power and the surface chemistry of the SiO₂/Si substrate on optical doping of exfoliated graphene in air is examined. Our result also implies that Raman spectroscopy of graphene performed with usual incident laser power density (around $\text{mW}/\mu\text{m}^2$) layers can be invasive as it directly alters the charge carrier density.

RESULTS

In a first series of experiments, Raman spectra of exfoliated graphene are collected as a function of the incident laser power, P_{laser} , at a fixed location. The results obtained for three different samples are compared. F1 was exfoliated on a hydrophilic SiO₂/Si substrate, F2 on

a less hydrophilic substrate and F3 was suspended over a trench etched into the substrate (see methods). The quality of the samples is preserved during the whole experiments, as evidenced by the absence of the D band (see Supplementary Fig. S1). All Raman spectra are fitted by Lorentzian functions to extract the position of the G band (ω_G), the full width at half maximum (FWHM) of the G band (Γ_G), the 2D band position (ω_{2D}) and the ratio between the integrated intensities of the 2D and G bands (A_{2D}/A_G). For the sample F1, P_{laser} is increased from 0.05 mW up to 1.5 mW and decreased back to 0.05 mW, as shown in Figure 1. The G band at 1580 cm^{-1} for $P_{\text{laser}} = 0.05 \text{ mW}$ downshifts to reach a minimum value 1576.5 cm^{-1} for $P_{\text{laser}} = 0.5\text{--}0.6 \text{ mW}$. With the further increase of P_{laser} , it upshifts up to 1579 cm^{-1} . Correspondingly, Γ_G , rises from 7 cm^{-1} up to 12 cm^{-1} for $P_{\text{laser}} = 0.5\text{--}0.6 \text{ mW}$ and then decreases to 10 cm^{-1} (Fig. 1b). In the same conditions, the 2D band continuously downshifts from 2666 cm^{-1} down to 2663 cm^{-1} (Fig. 1c). The A_{2D}/A_G ratio displays a maximum for P_{laser} around $0.5 - 0.6 \text{ mW}$ (Fig. 1d). Comparing the observed concomitant evolution of ω_G , ω_{2D} , Γ_G and A_{2D}/A_G with electrostatic gating results¹⁻⁴ indicates that the graphene doping is modified upon light irradiation. In particular, the coincidence of the maxima of Γ_G and of A_{2D}/A_G with the minimum of ω_G is a signature of neutral graphene. The doping type is determined from the evolution of ω_{2D} :^{3,4} larger upshift for P-doping (below $0.5 - 0.6 \text{ mW}$), than for low-level N-doping (above $0.5 - 0.6 \text{ mW}$). Interestingly, the changes are observed to be mostly reversible when P_{laser} is decreased back to its initial value (Fig. 1) so that the doping of graphene deposited on a hydrophilic SiO_2/Si substrate can be continuously and reversibly tuned from the initial P-doping to quasi-neutral and eventually N-doping with moderate laser power. From the shifts and widths of the G band^{3,4} the initial doping of F1 was estimated to be $p \approx 4 \times 10^{12} \text{ cm}^{-2}$ at 0.05 mW . For $P_{\text{laser}} = 1.44 \text{ mW}$, the carrier density was estimated to be $n \approx 3 \times 10^{12} \text{ cm}^{-2}$.

We now examine the influence of the underlying substrate by comparing these results to the ones obtained on sample F2 deposited on a less hydrophilic substrate and to sample F3 suspended over a trench etched into the substrate. The relative variations of the 2D and G band positions as a function of P_{laser} are collected in Figure 2. This particular representation disentangles doping and strain effects³³. We clearly observe three different behaviors in the plots presented on Figure 2. When the doping of graphene is continuously tuned from P-type to N-type (Fig. 1), the 2D versus G positions presents the particular v-shape shown in Figure 2a. The G band consistently upshifts with an increasing charge carrier density

(for both electrons and holes). The 2D band downshifts monotonically as the doping varies from P to N. Figure 2b displays the 2D vs G behavior for a flake lying on a less hydrophilic substrate. The G and 2D bands continuously upshift as P_{laser} increases. The small upshift of the 2D band is expected for low level N-type doping^{3,4,23}. Here, Γ_G is maximum for the lowest incident power and continuously decreases with the increasing laser power, and so does the A_{2D}/A_G ratio (see Supplementary Fig. S2). Considered together, these variations indicate that this supported graphene is close to neutral for the lowest P_{laser} and becomes N-doped as P_{laser} is increased (for $P_{\text{laser}} = 2.6$ mW, $n \approx 4 - 5 \times 10^{12} \text{ cm}^{-2}$ from refs. 3 and 4). Once again, these doping variations are reversible when P_{laser} is decreased back. For the suspended graphene flake, F3, the high values of Γ_G (14 cm^{-1}) and A_{2D}/A_G ratio (9.5) remains constant through the entire power sweep (Supplementary Fig. S3). This indicates that F3 remains neutral as the laser power increases in agreement with S. Berciaud *et al.*³⁵ Thus, the small shifts of ω_G and ω_{2D} (Fig. 2c) cannot be ascribed to any doping level variation.

We can now wonder how these laser induced doping variations are uniform across the graphene surface. To this end, Raman mapping was performed at different laser powers on graphene exfoliated onto a hydrophilic substrate and partially suspended over a pre-patterned trench (sample F4). Maps of the ω_G , Γ_G , ω_{2D} and A_{2D}/A_G are displayed on Figure 3 for seven P_{laser} ranging from $100 \mu\text{W}$ to 3 mW . The constant position of the G and 2D bands across the whole supported area of the sample indicates that the strain and doping are homogeneous, therefore allowing to single out the influence of optical doping by the varying laser power. When the laser power is increased from $100 \mu\text{W}$ to 1.5 mW , the G band, initially at 1584 cm^{-1} ($\Gamma_G = 7.5 \text{ cm}^{-1}$) shifts down to 1582 cm^{-1} ($\Gamma_G = 12 \text{ cm}^{-1}$). Further increase of the laser power inverts the effect and the G band upshifts back to 1582.5 cm^{-1} (Γ_G decreases down to 9.5 cm^{-1}). For the same power sweep, the 2D band continuously downshifts from 2676 to 2672 cm^{-1} . Similarly, the A_{2D}/A_G ratio increases from 4.7 for $P_{\text{laser}} = 100 \mu\text{W}$, to 5.1 for P_{laser} between 0.5 and 1.5 mW , and then decreases back to 4.7 for higher laser powers. These observations confirm that graphene supported on hydrophilic SiO_2 evolves continuously from P-type to N-type doped graphene when the laser power is increased.

Interestingly, the irradiation of the suspended graphene yields a very different behavior. Indeed, Figure 3 shows that both G and 2D bands downshifts from 1581.5 to 1578.5 cm^{-1}

and from 2673 to 2663.5 cm^{-1} respectively as the laser power is increased. However, Γ_G and the A_{2D}/A_G ratio remain constant (13 cm^{-1} and 5.9 respectively). Therefore the doping level remains unchanged through the entire power sweep and the downshifts of the 2D and G bands are ascribed to classical laser-induced heating effects that are also observed on samples F1 and F3 (see Supplementary Fig. S4).

A careful examination of the signals recorded on the graphene edges and on the trench contour reveals that the optical doping is less effective in these specific locations. In particular, the doping never reaches N-type even for the highest P_{laser} . We attribute this local effect to the supplementary P-doping near graphene edges which has already been observed by Raman spectroscopy^{39,40}.

DISCUSSION

The absence of doping upon irradiation of suspended graphene clearly shows that the substrate contributes to the mechanism involved in the optical doping of graphene. We thus investigated the influence of substrate cleaning procedures on the efficiency of the optical doping. For highly hydroxylated (hydrophilic) substrates freshly cleaned by O_2 plasma and/or Piranha treatments prior to graphene deposition, we observe the ambipolar behavior with a doping evolving from P-type to N-type upon increasing laser power. Our results confirm that graphene exfoliated on a hydrophilic substrate is P-doped^{41,42} in contrast to the quasi-intrinsic state of suspended graphene³⁵. Across the different samples studied here, we found that the P_{laser} for which graphene is neutralized falls in the range 0.5-1.5 mW. We anticipate that these values can change with the laser wavelength and the thickness of the SiO_2 layer. The density of hydroxyl groups can be reduced by performing a thermal annealing of the samples under argon before graphene deposition. In this case, graphene was observed to be initially quasi-neutral and N-type doping was obtained upon illuminating the sample with increasing P_{laser} . Finally, when graphene is transferred onto substrates used as-received without any cleaning, the doping of some flakes remain constant for all the entire P_{laser} range (not shown). Therefore, the absence of any significant spectral changes previously observed²⁴ might be accounted for by the deposition of graphene on as-received substrates. Finally, it should be pointed out that optical doping is not specific to graphene micromechanically exfoliated onto SiO_2/Si substrates but similarly occurs for graphene deposited on standard

glass (not shown)

It thus appears that the starting value of the graphene doping level is directly linked to the substrate preparation. Cleaning procedures that render the substrate hydrophilic tend to result in more P-doped supported graphene, in agreement with previous studies^{43–47}, which also demonstrated the involvement of adsorbed water in the P-doping of graphene by atmospheric oxygen^{36,42,45,47,48}. Irreversible or slow modulation of charge carrier density was demonstrated by changing the atmosphere^{36,42} or by illuminating graphene with UV or visible light^{36,37,49}. In the latter cases, the invoked mechanisms relied on UV photons or laser heating assisted removal of dopant molecules and more specifically oxygen derivatives. The characteristic times of such phenomena were found to be in the range of minutes^{36,49} or even hours³⁷. Other authors probed the dynamics of charge transfer between the H₂O/O₂ redox couple and graphene by electrical measurements alone or combined with Raman spectroscopy. It was shown that the equilibrium is established after minutes⁴⁸ or hours⁴².

Our study shows that the charge carrier density can be conveniently tuned by adjusting the incident laser power even without a gating electrode. This effect does not involve the chemical modification of graphene since no D band emerges upon extended irradiation. By contrast with previous reports^{36,37,49}, this laser-induced doping is reversible with a characteristic time that was preliminarily evaluated to be less than 1 s, *i.e.* orders of magnitude faster. This suggests that this phenomenon, although related to similar environmental effects, involves a different mechanism. O₂ and H₂O are playing a key role as illustrated by the weak dependency of ω_G on P_{laser} found after adsorbates removal by Ar annealing at 150°C of graphene lying on O₂ plasma treated SiO₂/Si substrates³⁴. Considering the H₂O/O₂ redox couple or O₂⁻ superoxide anion, it has been suggested that optically excited graphene transfers “hot” electrons³⁶. This would lead to an increase of hole doping in graphene upon visible light exposure, contrary to our observations. This suggests that other electrochemical reactions kinetically more favorable than the one considered previously might be involved. Noteworthy, graphene lying on SiO₂/Si exposed to H₂O alone, with only traces of O₂, has been shown to be N-doped⁴². Similarly, water significantly reduces hole doping of graphene deposited on mica⁵⁰. The elucidation of the laser assisted charge carrier density tuning mechanism is beyond the scope of this paper and deserves further investigation.

In conclusion, we have shown that a low power visible laser light can be used to reversibly tune the charge carrier density of graphene lying on a substrate. This effect is highly

sensitive to the substrate hydrophilicity and completely suppressed in suspended graphene. The continuous tuning of the doping in graphene from P-type to N-type has been achieved on O₂ plasma treated SiO₂/Si substrates. The observed sub-second dynamics of the optical gating phenomenon points to a new underlying mechanism that remains to be elucidated.

One technical implication of our study for the entire scientific community using Raman spectroscopy of graphene as a routine characterization technique is that it should be considered as potentially invasive as far as electronic properties are concerned. In particular, the laser induced-modification of graphene doping could account for recent discrepancies between Raman and electrical transport measurements⁴⁵. It would be interesting to extend the present work to graphene on metals⁴⁷ and on silicon carbide⁵¹ to assess how carefully Raman experiments on graphene must be performed.

On another hand, the ability to tune the charge carrier density with visible photons opens a wide set of opportunities to develop optically gated graphene electronic devices and a new approach to graphene optoelectronics. Finally, this effect should allow to study the interplay between graphene properties and the environment and to trigger laser-assisted functionalization of graphene leading to more advanced devices^{52,53}.

METHODS

Sample fabrication

Four samples (F1 through F4) were prepared for this study. The four of them consisted on a 500 μm thick highly P-doped monocrystalline Si (100) substrate, with a thermal oxide layer of 290 ± 5 nm (in F1 and F3, oxide grown in O₂; in F2 and F4, oxide grown in H₂O) and a square matrix of metallic marks every 200 μm to ease the identification of graphene flakes. Samples F3 and F4 were further processed by etching matrices of 5×1 μm trenches with depths of 160 nm (F3) and 480 nm (F4) in between the metallic marks with a CF₄ ICP-RIE process.

Cleaning of F1 and F3 was performed by sonication in organic solvents (N-methyl-2-pyrrolidone, acetone and isopropanol; VLSI quality), immersion in Piranha bath (H₂SO₄/H₂O₂ 3:1) during 3 hours and Ar/O₂ (3:1) plasma cleaning in a Fischione 1020 for 20 min. On the other hand, F2 and F4 were cleaned by sonication in organic solvents and O₂ plasma

cleaning in a PVA TePLA 300 at 800 W for 15 min. In addition, sample F2 was annealed during 1 hour at 400 °C in a 300 sccm Ar flow at atmospheric pressure.

Finally, graphene was deposited on all samples by exfoliation from kish graphite with the scotch tape method⁵⁴.

Micro-Raman spectroscopy

Raman spectra were recorded using an Acton spectrometer fitted with a Pylon CCD detector and a 600 grooves/mm grating (2.5 cm^{-1} between each CCD pixel). The samples were excited with a 532 nm (2.33 eV) CW frequency doubled Nd:Yag laser through a x100 objective (N.A. 0.9). The gaussian laser spot FWHM is about 350 nm. Optimized focus conditions have been checked for each measurement. The sample are mounted on a three-axis piezoelectric stage to ensure the precise positioning and focusing of the laser spot. The maps were recorded with a $0.2 \text{ }\mu\text{m}$ step in X ($0.4 \text{ }\mu\text{m}$ in Y) to probe the suspended graphene independently with a minimum of 2 to 3 points in the middle of the pool. The laser power was tuned with a variable neutral density filter controlled by a servomotor. The laser power was continuously measured by a calibrated photodiode put behind the beamsplitter. The whole experimental setup (spectrometer, piezoelectric stage, photodiodes, servomotor) were controlled by a dedicated and home-made Labview application.

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AUTHOR CONTRIBUTIONS

All authors contributed extensively to the work presented in this paper.

SUPPLEMENTARY INFORMATION

Optical microscopy (OM) images of the samples F1, F3 and F4 are shown. Raman spectra of F1 for three different laser powers are compared to the typical Raman spectrum collected on the suspended graphene flake F3. Raman spectra evolutions of F2 and F3 samples as a function of P_{laser} are displayed. Finally, evidences of laser-induced heating of the F1 and F3 samples are detailed.

COMPETING FINANCIAL INTERESTS

The authors declare no competing financial interests.

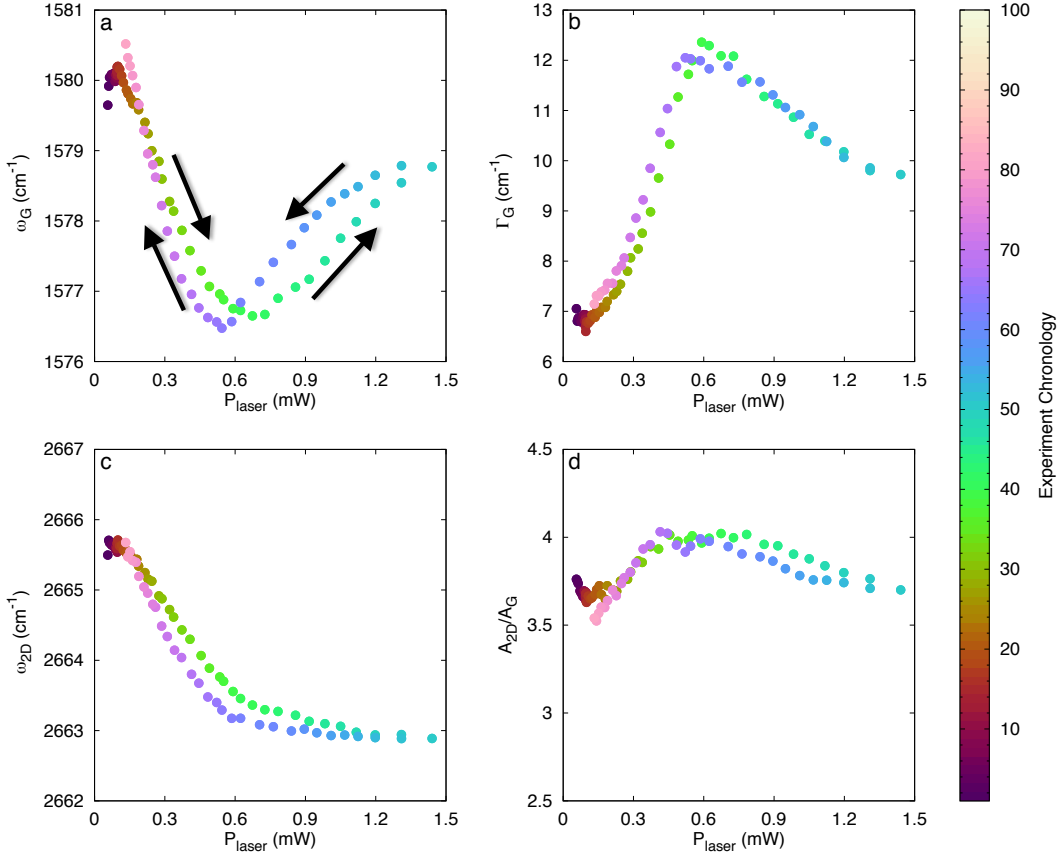


FIG. 1. **Reversible evolution of Raman spectra as a function of the incident laser power P_{laser} for the graphene flake F1.** a) the G band position ω_G , b) the G band FWHM Γ_G , c) the 2D band position ω_{2D} and d) the integrated intensities ratio A_{2D}/A_G . The graphene flake F1 is exfoliated on a hydrophilic substrate. P_{laser} is increased from 0.05 mW up to 1.5 mW and decreased back to 0.05 mW as shown by the arrows in (a). The color code of each point corresponds to the chronological order in which the measurements have been carried out as depicted on the right hand side color bar.

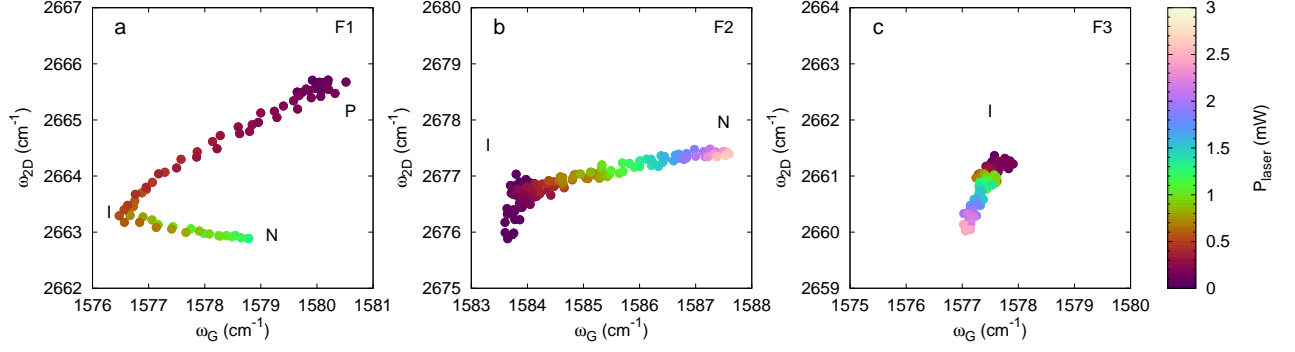


FIG. 2. Comparison of the relative evolutions of the 2D band position (ω_{2D}) versus the G band position (ω_G) as a function of P_{laser} for three graphene flakes (F1, F2 and F3). F2 was exfoliated on a less hydrophilic SiO_2/Si substrate than F1. F3 was suspended over a trench etched into the substrate. The color code of each point corresponds to the incident laser power P_{laser} as displayed on the right hand side color bar. a) F1 is P-doped at low P_{laser} , it becomes quasi-neutral around 0.5 mW and N-doped for higher P_{laser} . b) F2 is initially quasi-neutral and becomes N-doped with the increasing P_{laser} . c) The suspended graphene flake, F3, is neutral and stays neutral with the increasing P_{laser} . The measured shifts for F3 are only due to laser heating effects. The different G band and 2D band positions (ω_G , ω_{2D}) of the different graphene samples (F1, F2, F3) in their quasi-neutral state are attributed to strain fluctuations from one sample to the other.

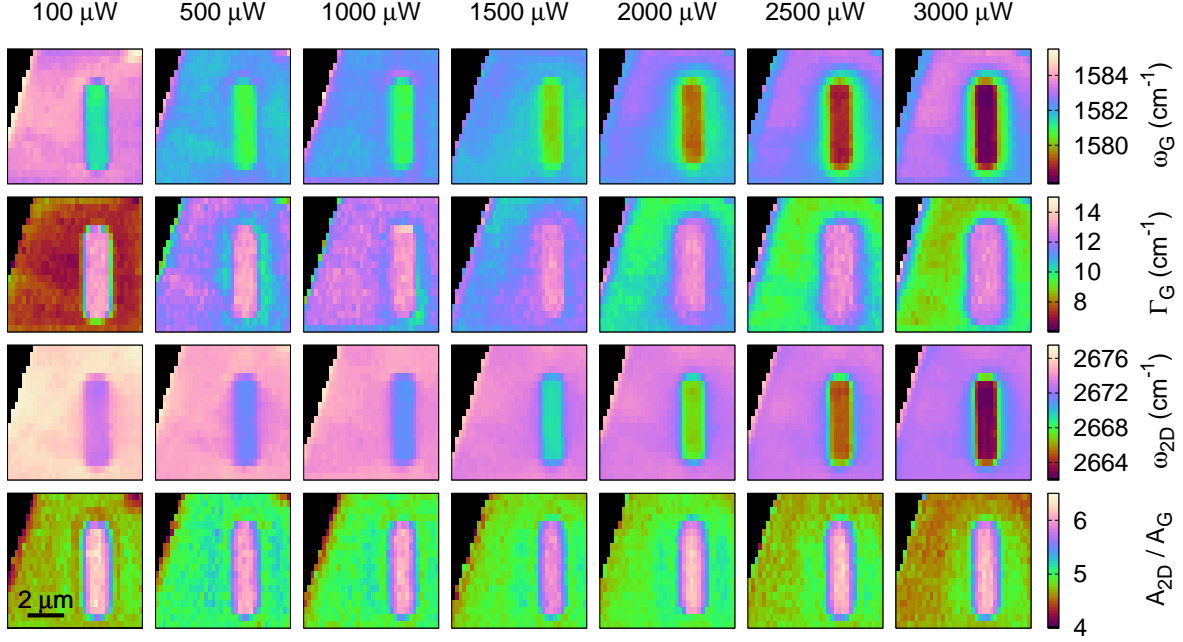


FIG. 3. **Raman maps measured for 7 different laser powers on sample F4.** The rows correspond from top to bottom to the G band position ω_G , the G band FWHM Γ_G , the 2D band position ω_{2D} , and the integrated intensities ratio A_{2D}/A_G . The graphene flake is covering an etched pool of the substrate that has a capsule shape and is visible on the right hand side of each map. The black upper left corners correspond to bare SiO $_2$ /Si surfaces.

Supplemental Information

Reversible optical doping of graphene

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Optical Microscopy images and Raman spectra of the graphene flakes

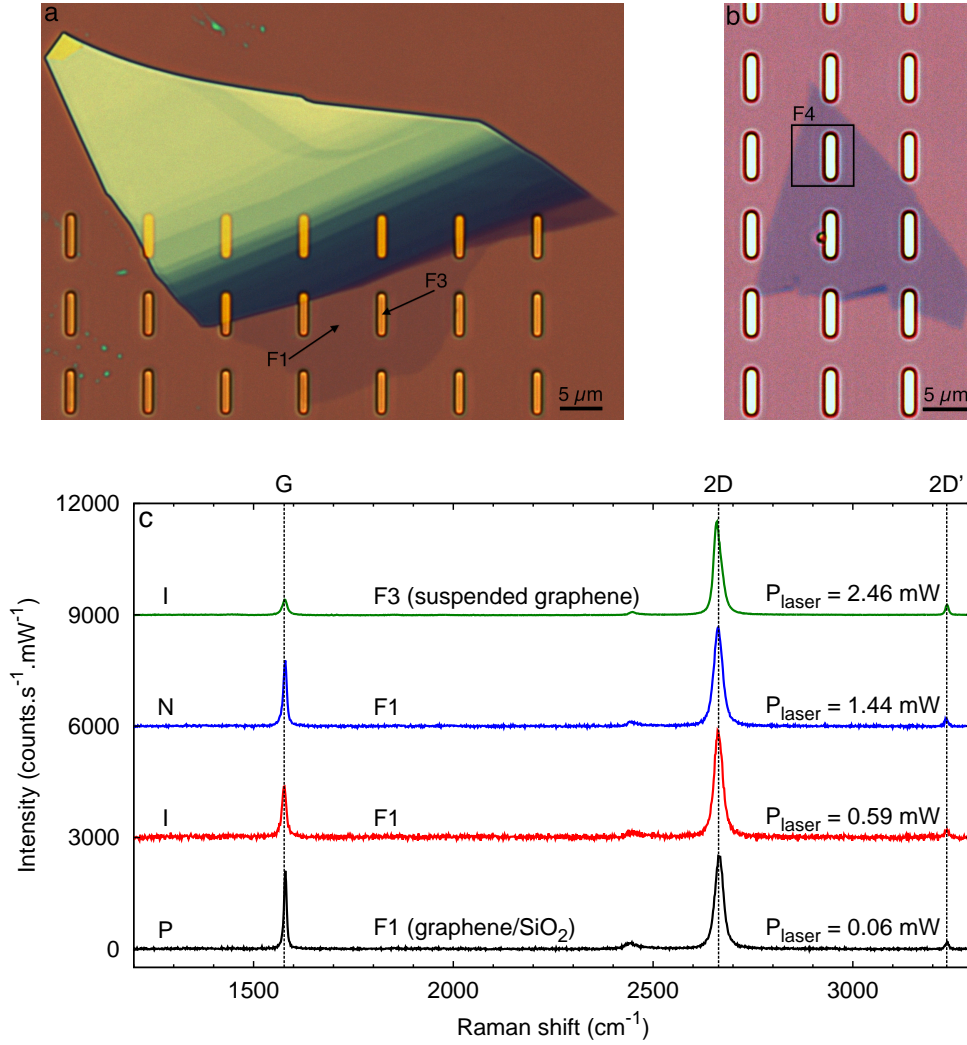


FIG. S1. **Optical Microscopy (OM) images and Raman spectra of the graphene flakes.**

a) OM of F1 and F3 b) OM of F4. The black square corresponds to the area mapped in Fig.3 c)

The Raman spectra of F1 for 3 different laser powers are compared to the typical Raman spectrum collected on the suspended graphene flake F3.

Raman spectra evolutions of F2 and F3 flakes as a function of P_{laser}

The graphene flake F2 is exfoliated on a less hydrophilic substrate than F1. P_{laser} is increased from 0.05 mW up to 2.6 mW and decreased back to 0.05 mW. The G and 2D bands continuously upshift as P_{laser} increases. For this sample, Γ_G is maximum for the minimum incident power and continuously decreases with the increase of P_{laser} , so does A_{2D}/A_G . The moderate ω_{2D} upshift indicates low N-doping^{3,4}. All these variations indicate that this graphene flake is quasi-neutral for the lowest P_{laser} and becomes N-doped as P_{laser} is increased ($n \approx 4 - 5 \times 10^{12} \text{ cm}^{-2}$ from refs. 3 and 4, for $P_{\text{laser}} = 2.6 \text{ mW}$).

For the suspended graphene flake, F3, the ω_G and ω_{2D} are almost constant as P_{laser} increases (Fig. S3). This suspended flake is neutral and stays neutral as the P_{laser} increases. It is confirmed by the constant Γ_G and the constant A_{2D}/A_G ratio (Fig. S3). The only small downshift of the G and 2D bands comes from the laser heating of the suspended flake (see the “Heating effect” section).

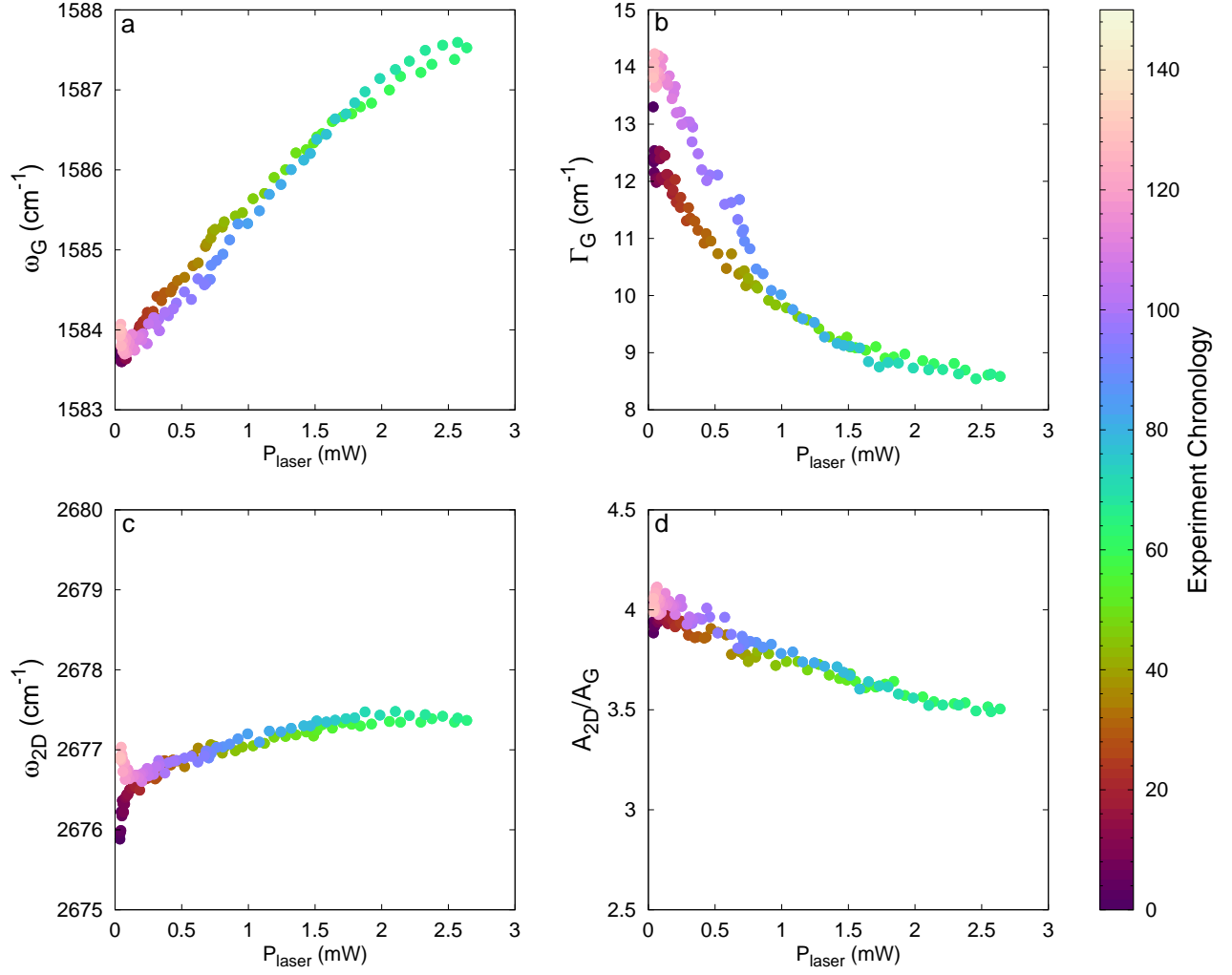


FIG. S2. **Reversible evolution of Raman spectra as a function of the incident laser power P_{laser} for the graphene flake F2.** a) the G band position ω_G , b) the G band FWHM Γ_G , c) the 2D band position ω_{2D} and d) the 2D/G integrated intensities ratio A_{2D}/A_G as a function of the incident laser power P_{laser} . F2 was exfoliated on a less hydrophilic substrate than F1. P_{laser} is increased from 0.05 mW up to 2.6 mW and decreased back to 0.05 mW. The color code of each point corresponds to the chronological order in which the measurements have been carried out as depicted on the right hand side color bar.

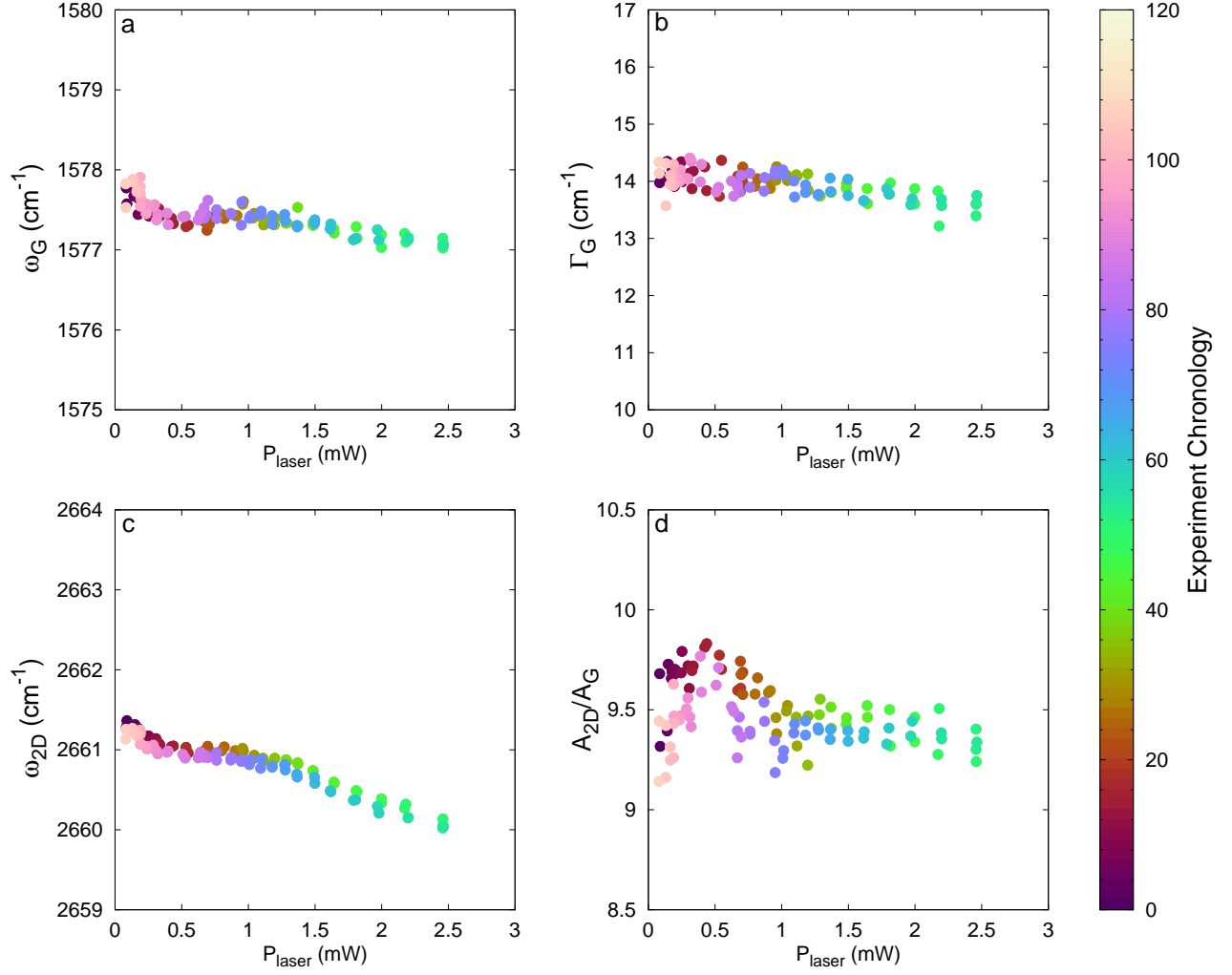


FIG. S3. **Reversible evolution of Raman spectra as a function of the incident laser power P_{laser} for the graphene flake F3.** a) the G band position ω_G , b) the G band FWHM Γ_G , c) the 2D band position ω_{2D} and d) the 2D/G integrated intensities ratio A_{2D}/A_G as a function of the incident laser power P_{laser} . F3 was suspended over a trench etched into the substrate. P_{laser} is increased from 0.05 mW up to 2.5 mW and decreased back to 0.05 mW. The color code of each point corresponds to the chronological order in which the measurements have been carried out as depicted on the right hand side color bar.

Heating effect

Fig. S4 displays how the 2D band FWHM (Γ_{2D}) and the 2D' band position ($\omega_{2D'}$) depend on the incident laser power P_{laser} . For the graphene flakes F1 and F3 the 2D band broadens and the 2D' band downshifts as P_{laser} increases. F. Alzina *et al.* showed that the 2D' band position does not depend on graphene doping level¹¹. Only strain and/or heating effects can induce such downshift. Moreover, it has been also shown that the 2D band linewidth depends linearly on the temperature⁵⁵. Assuming that inhomogeneous broadening of the 2D band do not evolve with P_{laser} , we can deduce that this 2D band broadening and 2D' band downshift are due for F1 and F3 sample to heating effects. In opposition, the graphene flake F2 do not exhibit P_{laser} dependance of Γ_{2D} and $\omega_{2D'}$. It means that this flake is not heated for this P_{laser} range, within the experimental precision.

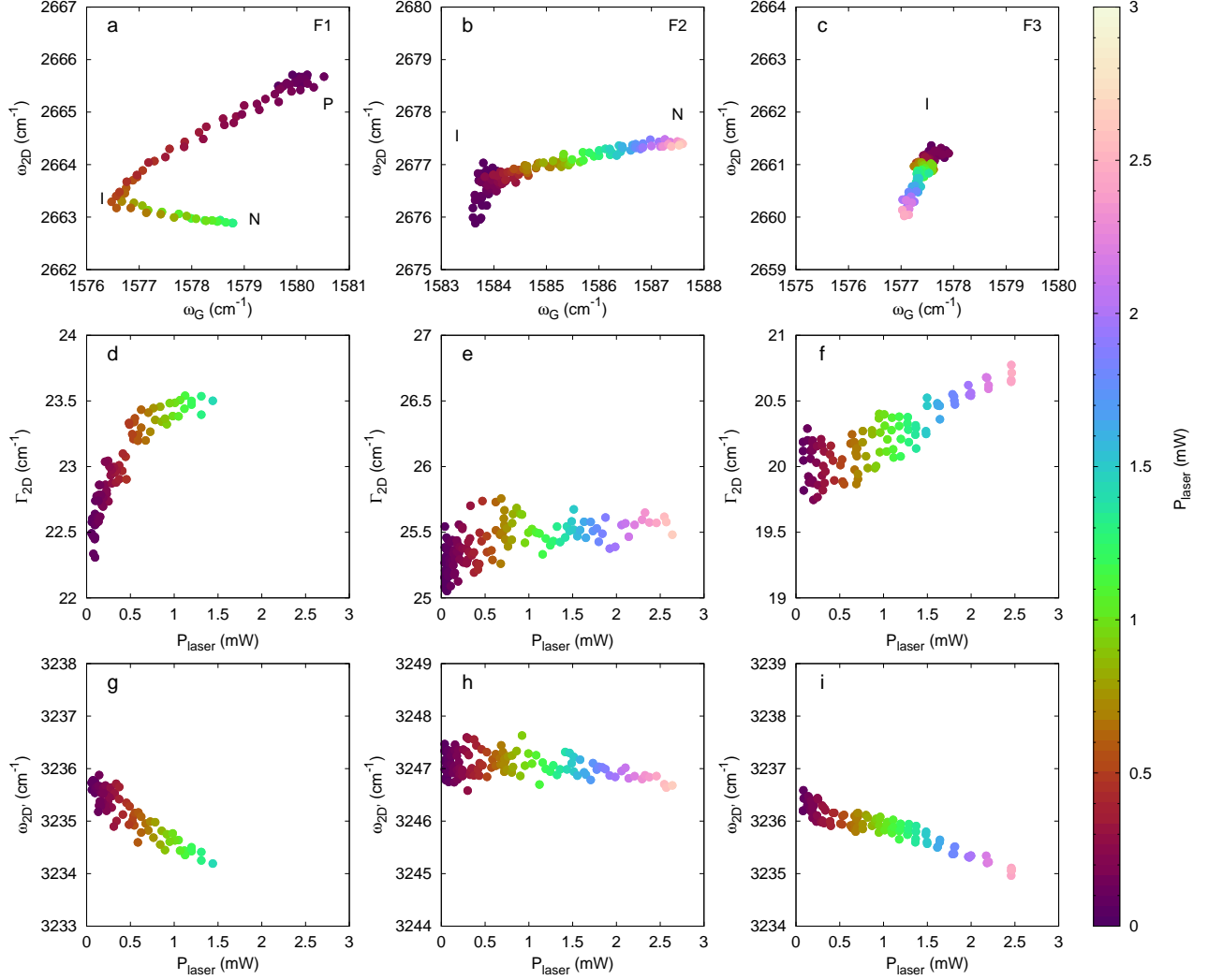


FIG. S4. **Raman fingerprint of a laser-induced heating effects.** Comparison of the relative evolutions of the 2D band position (ω_{2D}) versus the G band position (ω_G), the 2D band FWHM (Γ_{2D}) and the 2D' band position ($\omega_{2D'}$) as a function of P_{laser} for three graphene flakes (F1, F2 and F3). F2 was exfoliated on a SiO_2/Si substrate less hydrophilic than F1. F3 was suspended over a trench etched into the substrate. The color code of each point corresponds to the incident laser power P_{laser} as displayed on the right hand side color bar. For the graphene flakes F1 and F3 the 2D band broadens and the 2D' band downshifts as P_{laser} increases. These variations are ascribed to a laser induced heating. In opposition, the graphene flake F2 does not exhibit laser power dependance of Γ_{2D} and $\omega_{2D'}$ and is therefore not heated for this laser power range.